Synthesis of hollow silica nanoparticles using poly (acrylic acid)-3,3'-diaminodipropylamine template

Chika Takai Yamashita, Hiroshi Imabeppu, Masayoshi Fuji

Advanced Ceramics Research Center, Nagoya Institute of Technology

3-101-1 Honmachi, Tajimi, Gifu, 507-0033 Japan

fuji@nitech.ac.jp

TEL: +81-572-24-8110

FAX: +81-572-24-8109

Abstract

Synthesis of hollow silica nanoparticles using poly (acrylic acid) (PAA)-amine aggregates as nano-sized template was proposed. The PAA-amine mixtures dissolve in water, but not in ethanol, therefore the mixtures can be a template for hollow particle in ethanol and can be removed from the core-shell particle by addition of water. In order to investigate effect of amines on hollow particle formation, four kinds of amines; ethylenediamine (EDA), N,N,N',N'-tetramethylethylenediamine (TED), 3,3'-diaminodipropylamine (DDA), triethylenetetramine (TTA), which interact with carboxylic acid of PAA were chosen. The PAA-each amine nanoparticles were formed with around 200 nm by dropping of PAA/amine mixtures in ethanol under the optimum conditions. Using the PAA-DDA template, hollow silica nanoparticles with spherical form were successfully prepared for the shortest reaction time **in four hours**. The primary amines and secondary amine of DDA work as not only cross-linker for PAA, but also sol-gel reacting catalyst. It can be clear from that the EDA with two primary amines also worked as sol-gel catalyst while the TED with two tertiary amines didn't. On the other hands, TTA with two primary and secondary amines also provided hollow silica nanoparticles, however, the silica shell of particles were mostly collapsed. It could be thought that the four amines of TTA promote sol-gel reaction, at the same time, high water content in the template induces molecular motion.

Keywords: Hollow nanoparticle, poly (acrylic acid), silica, ammonia, 3,3'-diaminodipropylamine

1. Introduction

Hollow silica nanoparticles, which are composed of a solid silica shell and nano-sized hollow interior, can be expected to have unique properties of a high specific surface area [1-4], thermal insulation [5-7], optical property [8], nano-sized container [9, 10], etc. A lot of synthetic routes for hollow silica nanoparticles which are categorized into soft and hard templates were reported. In these template methods, silica source is firstly coated on the template surface to form core-shell particles, and then the template is removed by suitable chemical treatments such as combustion and dissolution. From the aspect of environmental issue, development and improvement of preparation technique for hollow silica nanoparticles are also important.

In the hard template methods, polystyrene (PS) particles were often used as the organic template because it is relatively easy to synthesis and control particle size [11]. At the same time, they have disadvantage of environmental load such as discharging waste harmful solvent to dissolve the template or carbon dioxide to burn off the template.

Fuji et al. developed inorganic template method using calcium carbonate (CaCO_3) or hydroxyapatite (HAp). These templates can be removed by dilute acid solution and the waste byproducts are re-used to re-synthesis the templates [12-14]. Min Chen developed one-step synthesis for hollow silica particle in which formation of silica shells and dissolution of the template particles occurs in the same medium. They controlled rates of silica coating and template removal by adjusting of ammonia amount in the medium [15, 16].

We focus on polyelectrolyte aggregation as nano-sized template for hollow particle, whose dissolution property can be controlled by just addition of water. Shi et al. synthesized polymeric nanoprecipitation using poly(allylamine hydrochloride) (PAH) in ethanol [17]. In Yu's group, poly(acrylic acid) (PAA)-ammonia nanoparticles were synthesized as hollow particle's template using the properties that PAA's insolubilization in ethanol under ammonia existence and solubilization in water. The PAA powder and ammonia solution were mixed and the solution was dropped in ethanol to make PAA-ammonia template/ethanol suspension. Tetraethoxysilane (TEOS) as a silica source was slowly added in the suspension and stirred at 2 hour intervals to prepare silica shell/PAA-ammonia template particles. By addition of distilled water, the PAA-ammonia template was removed. This process is simple without harmful influence on environment, however, it takes 14 hours long for silica shell coating on the template. There is no mention about a reason why that such long time is required [18].

Previously, we have obtained hollow silica nanoparticles by following of Yu's technique [19]. Then, effect of water in ethanol on the silica shell microstructure was reported. In this technique, PAA molecules were aggregated with ammonium ion in ethanol to be a template for hollow particle. The added TEOS was hydrolyzed with the ammonia and coated on the aggregated PAA molecules to form a silica shell. The PAA molecules could be movable in ethanol and the template surface seems

to be quite unstable for stable attachment of the hydrolyzed TEOS. To solve these problems, it is necessary to accelerate silica coating or to harden the template. As former, an increase in TEOS or ammonia as a catalyst are required, while as latter, addition of as like a cross-linker to connect PAA molecules each other. Here, four kinds of amine compounds with various combinations of primary, secondary, tertiary amines were used and the effects of these amines on hollow structure formation were discussed.

2. Experimental section

2-1. Preparation of hollow silica nanoparticle

Hollow silica nanoparticles using PAA-ammonia template were prepared according to Yu's research [18]. A 0.09 g of PAA powder (molecular weight: 5000, Wako Pure Chemical Industries, Ltd.) and 25% ammonia solution (Wako Pure Chemical Industries, Ltd.) or 30% amines solutions (ethylenediamine (EDA, Wako Pure Chemical Industries, Ltd.), N,N,N',N'-tetramethylethylenediamine (TED, Wako Pure Chemical Industries, Ltd.), 3,3'-diaminodipropylamine (DDA, Tokyo Chemical Industry Co., Ltd.), triethylenetetramine (TTA, Wako Pure Chemical Industries, Ltd.) were mixed for 2 minutes. The solutions were completely dissolved which were visually confirmed. The mixed solutions were dropped in dehydrated ethanol (99.5%, Wako Pure Chemical Industries, Ltd.) and stirred. A 0.15 ml of tetraethoxysilane (TEOS, Wako Pure Chemical Industries, Ltd.) was added at 2 hours interval. The total reaction times were from 4 to 14 hours. After the desired times of stirring, the suspensions were rinsed by ethanol and water, centrifuged and dried under vacuum atmosphere.

2-2. Characterizations

For microscopic observation, the obtained samples dispersed in ethanol were immobilized on a microgrid and observed by transmission mode of a scanning electron microscope (STEM, SEM, JSM-7600F, JEOL Ltd.). The viscosity of the PAA-amines solutions were measured by HAAKE Rheo Stress 6000 (Thermo Fisher Scientific K.K.). The particle size of PAA-amines template in ethanol was measured by zetasizer (Malvern Instruments Ltd).

3. Results and discussion

Figure 1(a) shows SEM observation of PAA-ammonia template by dropping of PAA (0.09 g) and ammonia (1.5 ml) mixture in ethanol (30 ml). The PAA-ammonia templates were formed as gathering of large particles with over 100 nm and small ones with less than 100 nm. According to Yu's research, one of the factors to dominate the template size is PAA amount for ammonia. It can be controlled from several tens nm to hundreds nm [18]. In our experiment, mechanical treatment is also effective. The results will be appeared elsewhere.

Using the above PAA-ammonia template, effect of reaction time on hollow particle formation was investigated. Figure 1(b)-(d) shows STEM observations of samples which were prepared for (b) 8 hours, (c) 10 hours, and (d) 14 hours. For less than 8 hours, nothing was observed by microscope. For 8 hours reaction, there were very few particles observed. As shown in Fig. 1(b), partially-collapsed hollow particles which were caught on the microgrid were observed. The size of the obtained particles was less than 100 nm. For 10 hours reaction (Fig. 1(c)), the number of observed particles quite increased compared to ones for 8 hours (Fig. 1(b)). The large hollow particles with over 100 nm were also obtained in addition to the small ones with less than 100 nm, however, shell of the large hollow particles were broken (represented as arrows in the picture). For 14 hours reaction (Fig. 1(d)), the large and small hollow particles were clearly observed without collapsed. From these results, 14 hours reaction time is necessary to form hollow structures.

When TEOS were added in the PAA-ammonia template/ethanol suspension, TEOS molecules approach to the template and were hydrolyzed by the ammonia. The hydrolyzed TEOS were subsequently condensed by the ammonia and formed a silica shell at the template surface. In the PAA-ammonia template, templates can be formed by the interaction between ammonia and carboxylic acid (COOH) of PAA. The number of the added ammonia is over thousand times higher than the number of COOH of PAA. The excess of ammonia which were not used for the reaction with PAA played as a catalyst for hydrolysis and condensation of TEOS. However, the reaction of TEOS at the template surface is really slow. In addition, it can be thought that PAA molecules are movable in the PAA-ammonia solution template. The template surface could be unstable in ethanol and it seems to be difficult for quick attachment of the hydrolyzed TEOS. **The driving force of silica coating on the template surface is not clear. At the unstable template surface, ethanol, water, ammonia are mixed together because they are immiscible each other. Just after TEOS addition, hydrophobic TEOS exist in ethanol. If TEOS attaches ammonia near the surface, hydrolysis will be started. The hydrolysis TEOS prefer to stay in the hydrophilic template surface.**

To accelerate TEOS reaction, effect of ammonia amount on particle formation was investigated. Figure 2 shows STEM observations of particles prepared with increased in ammonia of a) 2.0, b) 2.5, c) 3.0, d) 6.0 ml. The PAA amount was constant as 0.09 g. With addition of 2.0 ml of ammonia (Fig. 2(a)), small hollow particles were observed without large ones as observed in Fig. 1(b) (1.5 ml of ammonia). It seems that the shell thickness increased. With increase in 2.5 ml (Fig. 2(b)), similar size of hollow particles (as an inserted figure) and dense particles were observed. The shell thickness of the hollow particles seems increase compared to Fig. 2(a). When addition of 3.0 ml (Fig. 2(c)), no hollow particles were observed. The obtained particles are rather porous than dense. With farther increased in 6.0 ml (Fig. 2(d)), another small dense particles were formed.

For understanding the above results, effects of ammonia amount on template size and viscosity were investigated. Figure 3(a) shows change in the PAA-ammonia template size in ethanol as a

function of ammonia. The Z-average size indicated over 200 nm with addition of 1.5 ml, it decreased rapidly to 50 nm with 2.5 ml of ammonia and then gradually decreased. Figure 3(b) shows change in viscosity of PAA-ammonia solution as a function of ammonia. It showed similar decrease behavior to the template size change in Fig. 3(a).

With increase in ammonia solution, the PAA-ammonia template size decreased because viscosity of the template solution decreased. As a result, the obtained hollow particle size also decreased (from Fig. 1(b) to Fig. 2(a)). With increase in ammonia, the PAA molecules seems much more movable because of increase in water content in the template. The boundary between the template and ethanol could be unidentified. If TEOS is hydrolyzed at the template surface, the hydrolyzed TEOS is hard to stay and condense each other at the surface. The hydrolyzed TEOS grows and gather to be porous particles (Fig. 2(b)(c)). With farther increase in ammonia solution, unreacted ammonia could be released to ethanol. The observed another small particles were formed by the ammonia which existed outside the template. From these results, increase in ammonia solution is not solution to shorten reaction time for hollow silica particles.

With the aim of increase in hardness of the template, four kinds of amines were chosen as cross-linker of PAA molecules through the reaction of amino groups and COOH of PAA. Chemical structures of the used four amines were shown in Figure 4. Ethylenediamine (EDA) (Fig. 4(a)) and N,N,N',N'-tetramethylethylenediamine (TED) (Fig. 4(b)) have two terminal amino groups in the main ethylene chain. Additionally, TED has two methyl groups at the terminal amino groups. 3,3'-diaminodipropylamine (DDA) (Fig. 4(c)) and triethylenetetramine (TTA) (Fig. 4(d)) have two terminal amino groups, and another one and two amines in the main chain, respectively. Summarizing the above, EDA has two primary amines, TED has two tertiary amines, DDA has one secondary amine with two primary amines, and TTA has two secondary amines with two primary amines.

Firstly, optimum quantities of each amine solution to prepare PAA-amines template were investigated. Table 1 shows synthetic conditions of 30 mass% amine solutions which were mixed with PAA (0.09 g) to prepare PAA-amines templates. The "condition" column in the table indicates ratio of number of amines per COOH between ammonia and the used amines. That is, the condition "1" means that the same amine/COOH ratio to the preparation condition of Figure 1(a).

When compared with (a) EDA, (b) TED, (c) DDA, similar changes were observed with increase in the amine solutions. In condition "1", there were large aggregations formed which can be visually confirmed without PAA-amine template formation. When the amine solutions were added twice, as condition "2", nano-sized templates were successfully prepared using the all three amine solutions. The Z-average particle sizes were similar as (a) 220, (b) 200, (c) 190 nm, respectively. When added three times, as the condition "3", only clear solutions were formed in the all three. The template formations were not also confirmed by particle size analysis. The viscosity of these three

PAA-amines solutions were listed in Table 1. Change in the viscosity of the all three solutions showed similar decrease with increase in amine solution in the order of 1, 2, and 3.

The large aggregation observed in the condition “1” seems to be caused by less soluble of PAA in the three amine solutions. The high viscosities in the condition “1” were caused by PAA molecules’ strong inter- and intra-aggregations. In the three times amine solutions in the condition “3”, it seems that PAA molecules totally dissolved without formation of PAA-amines interaction. The relative viscosities of (a) EDA, (b) TED, and (c) DDA solutions before addition of PAA were (a) 2.9, (b) 2.9, and (c) 3.6 mPas, respectively. These viscosities are almost same as that of PAA-amine solutions after addition of PAA ((a) 4.0, (b) 4.0, (c) 5.0 mPas). Therefore, it seems that the interaction between PAA and amines were not promoted in the condition “3”.

Secondarily, synthesis of hollow particles using PAA-three amines template of condition “2” was attempted. Figure 5 shows STEM observations of samples prepared using (a) EDA, (b) TED, and (c) DDA as the cross-linker of PAA for 4, 6, and 8 hours reaction times. When using EDA, nothing was formed for 4 hours and spherical hollow particles were formed for over 6 hours ((a)-1, 2). While using TED, nothing was observed for whole reaction time.

In condition “2” of EDA and TED, amount of these amines were two thousand times higher against one COOH of PAA. The free EDA which exists in the PAA-EDA template without cross-linking can work as catalyst for TEOS hydrolysis and condensation. However, the free TED couldn’t play as an effective catalyst for the TEOS reaction. Though both amines contribute to PAA aggregation formation and the aggregation sizes were similar, the relative viscosity of the PAA-EDA solution (41.0 mPas) was higher than that of PAA-TED solution (6.0 mPas). It seems that interaction of tertiary amines of TED with PAA is weaker than that of primary amines of EDA. From these results, the tertiary amines are not adequate for cross-linking agent of PAA.

When DDA with two primary amines and one secondary amine was used as cross-linking agent, 4 hours reaction provided hollow silica nanoparticles (Fig. 3(c)-1). The observed particles were about 10 nm in their size. After 6 hours reaction (Fig. 3(c)-2), large hollow particles with around 100 nm were formed in addition to the small one. For 8 hours reaction (Fig. 3(c)-3), the size of the hollow particles was not significantly changed. A single nanosized particles were newly observed.

The relative viscosity of the PAA-DDA solution was 100.0 mPas which is much higher value than that of PAA-EDA (41.0 mPas). It indicates that interaction between PAA and DDA is stronger than the other two amines. In the PAA-DDA template, enough amount of amines for TEOS hydrolysis and condensation could exist. At the boundary of the template and outer-phase ethanol, replacement of water, DDA, ethanol could be caused by a certain level of molecular motion. For longer reaction time such as 8 hours, dense silica particles were formed using excess free-DDA as catalyst in the outside ethanol.

In the three amines of EDA, TED, and DDA, DDA with two primary amines and one secondary

amine was the most effective to form PAA template and hollow particle for short reaction time. It seems that primary and secondary amines could work as not only cross-linker for PAA but also catalyst for TEOS reaction.

With aim of further reducing reaction time, TTA with two primary amines and two secondary amines was used. The chemical structure was shown in Figure 3(d). Table 1(d) shows synthetic condition to prepare PAA-TTA template and particle size analysis. In the conditions 1-3, large aggregations were formed owing to less soluble of PAA. The condition "4" provided PAA-TTA template nanoparticles with 190 nm in their size. With further increase in the TTA solution as the condition "5", the template was not formed because of completely soluble of PAA. Using the PAA-TTA template prepared under condition "4", synthesis of hollow particles were attempted. Figure 4(d)-1, 2, 3 shows STEM observations of the obtained samples for 4, 6, and 8 hours reaction, respectively. For 4 hours ((d)-1), only silica product like thin film was formed without hollow particle formation. For over 6 hours ((d)-2, 3), hollow particles with collapsed shell were formed. The particle size was not changed significantly with increase in the reaction time from 6 to 8 hours.

Although TTA has four effective amines, which can construct strong connection with PAA and good catalyst for TEOS reaction, the obtained hollow particles were mostly collapsed. The reason is still under investigation, but it can be thought due to followings. From the results of Table 1(d), relative large amount of water is required to prepare the PAA-TTA nanoparticles. The free TTA in the template promotes TEOS reaction, however, the formed silica shell can be weakened by the movable template surface.

4. Conclusion

The effects of four kinds of amines as EDA, TED, DDA, TTA on silica coating on PAA-amine templates were investigated. All the amines produced nano-sized template with around 200 nm, however, variety of amines in the four significantly affected silica coating formation. Using the PAA-DDA template, hollow silica nanoparticles with spherical form were successfully prepared for the shortest reaction time in the four amines. From rheological analysis of the template solution, DDA seems to work as effective cross-linker for PAA molecules. In addition, DDA promotes silica coating on the template as sol-gel reacting catalyst.

References

- [1] Masayoshi Fuji, Chika Takai, Yoshie Tarutani, Takashi Takei and Minoru Takahashi, Surface properties of nanosize hollow silica particle on a molecular level, *Advanced Powder Technology* 18(1) (2007) 81–91.
- [2] Jing Hu, Xuge Wang, Liqin Liu, Limin Wu, A facile and general fabrication method for organic silica hollow spheres and their excellent adsorption properties for heavy metal ions, *Journal of*

Materials Chemistry A, 2 (2014) 19771-19777.

[3] Yuyong Yin, Min Chen, Shuxue Zhou, Limin Wu, A general and feasible method for the fabrication of functional nanoparticles in mesoporous silica hollow composite spheres, Journal of Materials Chemistry, 22 (2012) 11245-11251.

[4] Manickam Sasidharan, Dian Liu, Nanda Gunawardhana, Masaki Yoshio, Kenichi Nakashima, Synthesis, characterization and application for lithium-ion rechargeable batteries of hollow silica nanospheres, Journal of Materials Chemistry, 21 (2011) 13881-13888.

[5] Qin Yue, Yuanzhi Li, Ming Kong, Jichao Huang, Xiujian Zhao, Jun Liu and Ralph E. Willifor, Ultralow density, hollow silica foams produced through interfacial reaction and their exceptional properties for environmental and energy applications, Journal of Materials Chemistry 21 (2011) 12041-12046.

[6] Masayoshi Fuji, Chika Takai, Hideo Watanabe, Kyoichi Fujimoto, Improved transparent thermal insulation using nano-spaces, Advanced Powder Technology, 26(3) (2015) 857–860.

[7] Yuchao Liaoa, Xiaofeng Wu, Haidi Liu, Yunfa Chen, Thermal conductivity of powder silica hollow spheres, Thermochimica Acta, 526(1-2) (2011) 178-184.

[8] Yi Du, Lunet E. Luna, Wui Siew Tan, Michael F. Rubner, Robert E. Cohen, Hollow silica nanoparticles in UV-visible antireflection coatings for poly(methyl methacrylate) substrates, ACS Nano, 4(7) (2010) 4308-4316.

[9] Kunlin Chen, Shuxue Zhou, Shu Yang, Limin Wu, Fabrication of all-water-based self-repairing superhydrophobic coatings based on UV-responsive microcapsules, Advanced Functional Materials, 25 (2015) 1035-1041.

[10] Shunsheng Cao, Long Fang, Zhiyuan Zhao, Yi Ge, Sergey Piletsky, Anthony P. F. Turner, Hierachically structured hollow silica spheres for high efficiency immobilization of enzymes, Advanced Functional Materials, 23 (2013) 2162-2167.

[11] Frank Caruso, Rachel A. Caruso, Helmuth Möhwald, Nanoengineering of inorganic and hybrid hollow spheres by colloidal templating, Science, 282(5391) (1998) 1111-1114.

[12] Masayoshi Fuji, Chika Takai, Yoshie Tarutani, Takashi Takei, Minoru Takahashi, Surface properties of nanosize hollow silica particles on the molecular level, Advanced Powder Technology, 18(1) (2007) 81-91.

[13] Masayoshi Fuji, Takahiro Shin, Hideo Watanabe, Takashi Takei, Shape-controlled hollow silica nanoparticles synthesized by an inorganic particle template method, Advanced Powder Technology, 23(5) (2012) 562–565.

[14] Raymond V. Rivera Virtudazo, Hidekazu Tanaka, Hideo Watanabe, Masayoshi Fuji, Takashi Shirai, Facile preparation in synthesizing nano-size hollow silicate particles by encapsulating colloidal-hydroxyapatite nanoparticles, Journal of 2015Materials Chemistry, 21 (2011) 18205-18207.

- [15] Min Chen, Limin Wu, Shuxue Zhou, Bo You, A method for the fabrication of monodisperse hollow silica spheres, *Advanced Materials*, **18**(6) (2006) 801–806.
- [16] Ziwei Deng, Min Chen, Shuxue Zhou, Bo You, Limin Wu, A novel method for the fabrication of monodisperse hollow silica spheres, *Langmuir*, **22** (2006) 6403-6407.
- [17] Yan Shi, Chika Takai, Masayoshi Fuji, Preparation of hollow silica particles templated by cationic polyelectrolyte aggregates, *Journal of Nanoscience and Nanotechnology*, accepted.
- [18] Yong Wan, Shu-Hong Yu, Polyelectrolyte controlled large-scale synthesis of hollow silica spheres with tunable sizes and wall thicknesses, *Journal of Physical Chemistry C*, **112** (10) (2008) 3641–3647.
- [19] Masayoshi Fuji, Chika Takai, Hiroshi Imabeppu, Xinhua Xu, Synthesis and shell structure design of hollow silica nanoparticles using polyelectrolyte as template, *Journal of Physics: Conference Series*, **596** (2015) 012007-012012.

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Figure 1 (a) SEM observation of PAA-ammonia template. (b)-(d) STEM observations of samples prepared using the PAA-ammonia template for different reaction times, (b) 8 hours, (c) 10 hours, and (d) 14 hours. **Scale bars are 100 nm.**

Figure 2 STEM images of PAA-removed-samples prepared with increase in ammonia solution of a) 2.0 ml, b) 2.5 ml, c) 3.0 ml, and d) 6.0 ml which were added to 0.09 g of PAA. Scale bars are 100 nm.

Figure 3 Change in (a) average particle size of PAA-ammonia template in ethanol and (b) relative viscosity of PAA-ammonia solutions with increase in ammonia solution.

(a)

(b)

(c)

(d)

Figure 4 Chemical structures of the used amines; (a) EDA, (b) TED, (c) DDA, and (d) TTA.

Table 1 Synthetic conditions of PAA-each amines solution and Z-average size of the template in ethanol.

Amines	Condition	PAA [g]	Amine solution [ml]	Template size [nm]	Relative viscosity of PAA-amines solution [mPa·s]
(a) EDA	1	0.09	0.27	>1 mm	400.0
	2		0.54	220 nm	41.0
	3		0.81	Not detected	4.0
(b) TED	1	0.09	0.54	>1 mm	380.0
	2		1.08	200 nm	6.0
	3		1.62	Not detected	4.0
(c) DDA	1	0.09	0.65	>1 mm	500.0
	2		1.30	190 nm	100.0
	3		1.95	Not detected	5.0
(d) TTA	1	0.09	0.64	> 1 mm	
	2		1.28		
	3		1.93		
	4		2.57	190 nm	
	5		3.22	Not detected	

Table 2 STEM observations of PAA-removed samples which were prepared using (a) DDA, (b) TED, (c) DDA, and (d) TTA, respectively. The scale bars are 100 nm.

Amines	Reaction time		
	4 hours	6 hours	8 hours
(a) EDA	Nothing formed	(a)-1	(a)-2
(b) TED	Nothing formed		
(c) DDA	(c)-1	(c)-2	(c)-3
(d) TTA	(d)-1	(d)-2	(d)-3

*Graphical Abstract